



## Mechanical properties and corrosion resistance of two new titanium alloys for orthopaedics applications

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### ABSTRACT

Due to the compatibility problems of biomaterials currently used in biomedicine, the effect of Silicon addition to the innovative TiMoZr alloy has been investigated. The mechanical properties of these two alloys and their corrosion resistance in simulated body fluid were analyzed in order to recommend them for the manufacture of medical instruments. After the application of the corresponding techniques, the metallographic study shows only the two-phase structure of the sample with silicon, which has lower modulus of elasticity values and higher Vickers microhardness values. The sample without silicon offers a higher resistance to corrosion, although these values between the two samples are very close.

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### 1. Introduction

Biomaterials are natural or synthetic materials that are used to fabricate structures or implants with the aim of replacing lost or diseased biological structure and restoring their form and function [1,2]. In recent years, advances in medicine and materials processing have enabled the development of many biomaterials containing suitable properties for various medical applications such as orthopaedics, drug delivery, dentistry, skin tissue engineering and cardiovascular devices, among others [1,3]. In this way, the quality of life and longevity of people can be improved. In turn, these biomaterials can be classified into metals, ceramics, polymers and composites [1,2,4].

In order to consider any material as an implant, the first thing to be taken into account is that the material is biocompatible with the human body, i.e. that it does not release toxic substances into the body as these can cause systemic damage to the patient; the second requirement is that it does not cause inflammatory or allergic reactions in the human body, it must not be carcinogenic, it must not cause rejection phenomena in the body, it must not alter the

composition of the blood or disrupt the coagulation mechanism, it must not change the biological pH, it must not contain hydrophobic sites that favour cell penetration and adhesion, and it must not contain any other substances that may be harmful to the patient's health [1,4,5].

In addition, these biomaterials must have superior corrosion resistance in the body environment, an excellent combination of high strength and low modulus of elasticity close to that of the cortical human bone ranging from 7 to 30 GPa [6], high fatigue and wear resistance, high ductility and absence of cytotoxicity to avoid loosening of the implants and to achieve a longer period of service, thus avoiding revision surgery, as well as the implant integrating well with the adjacent bone and developing good osseointegration [1,3].

Currently, within orthopaedic surgery, it is necessary to develop hip prostheses made mainly of metallic materials, as there is no plastic or ceramic that can support 10 times the weight of a person, so the heavier a person is, the more weight the hip will support. However, the modulus of elasticity of metals, about 200 GPa, is much higher than that of bone.

Also, few metals are suitable for use as permanent implants because of the toxic effect of released ion on surrounding tissues. However, these biocompatibility problems can be reduced by alloying the base metal with elements that do not show adverse

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effects on the organism [2,4]. On the other hand, metals are noted for their high tensile strength, high toughness and reasonable fatigue life, but their Young's modulus values are high compared to those of human bone [4].

The most commonly used metallic materials for medical applications are 316L stainless steel, CoCrMo alloys, Ti, Ti-based alloys such as Ti<sub>6</sub>Al<sub>4</sub>V and NiTi alloys [7,8]. Unfortunately, these materials have shown a tendency to fail after prolonged use due to several reasons, such as their high modulus compared to bone, low wear and corrosion resistance and lack of biocompatibility [1,9].

Titanium is widely used in a variety of applications due to the possibility of changing its properties by changing the composition of the alloying elements [4,6,10]. In addition, titanium and its alloys have prevailed over other conventional metals because they have the optimal characteristics required for implant materials, such as good mechanical properties, corrosion resistance and biocompatibility with biological materials. This biocompatibility is due to its low electrical conductivity, which contributes to the electrochemical oxidation of titanium as a very stable, thin passive oxide film forms and develops naturally on the surface of the material. This results in a high corrosion resistance of the material [3,5,11–17]. Nonetheless, the young modulus of elasticity of pure titanium is about 110 GPa and causes a stress shielding effect between the implant and the bone [8].

In general, titanium-based alloys have good properties and three types of titanium-based alloys are known:  $\alpha$ ,  $\alpha + \beta$  and  $\beta$  titanium. Pure titanium has an alpha structure, hexagonal compact structure (HCP), and becomes beta when heated above 882 °C by undergoing an allotropic transformation and changing its crystallisation system from hexagonal to body-centred cubic (BCC). However, in many alloys of this element, the beta phase can be maintained at room temperature, which means having a material containing both phases. In addition, the relative amounts of these phases produce variations in the properties of the alloy, such as ductility, plasticity or formability. Elements such as Mo, V, Nb and Ta are  $\beta$ -stabilising elements that decrease the temperature of allotropic transformation and neutrals such as Zr [4,18–20].

Although Ti-6Al-4 V alloy has been predominantly used throughout history, it has significant toxicity, as it causes harmful tissue reactions caused by vanadium and the release of vanadium and aluminium ions, leading to certain long-term health disorders, such as peripheral neuropathy, dementia, Alzheimer's and Parkinson's diseases and adverse tissue effects [9,21–23].

Then, recently, several researchers have tried to improve the properties of titanium by introducing non-toxic elements, such as Nb, Zr, Mo, Ta, etc. to improve surface characteristics, mechanical properties, corrosion resistance and biocompatibility, among others, obtaining new alloys such as Ti-13Nb-13Zr, Ti-5Al-2.5Fe, Ti-6Al-7Nb, TiMo, Ti<sub>36</sub>Nb<sub>2</sub>Ta<sub>3</sub>Zr, Ti<sub>24</sub>Nb<sub>4</sub>Zr<sub>7.8</sub>Sn, TiMoZrTa, Ti-Ta, TiMoZrTaSi and TiMoSi [18,24–26].

Molybdenum is a less toxic element compared to conventional metals such as Co, Ni and Cr. It is a  $\beta$ -stabilising element and therefore lowers the transition temperature from the  $\beta$ -structure to the  $\alpha$ -structure and stabilises the  $\beta$ -phase. This temperature is increased by the presence of  $\beta$ -phase stabilising alloying elements and, in many cases, is lower than room temperature, so alloys with this characteristic have a  $\beta$  in use at room temperature. In addition, some studies indicate that the addition of molybdenum results in mechanical properties similar to those of human bone [2,12,18,27].

Silicon is an element found in human bone and it is considered biocompatible as it increases corrosion resistance, reduces ductility, improves creep and high temperature resistance. Like molybdenum, it is a  $\beta$ -stabilising element that influences the decrease in modulus of elasticity [12,18,28].

Zirconium is starting to be used as an attractive option for most medical applications. It has a low modulus of elasticity, high corro-

sion resistance and high biocompatibility with human tissues. In addition, the zirconium alloy has lower magnetic properties than Ti alloys, Co-Cr alloys and stainless steels when exposed to magnetic fields from MRI devices [18,28–30].

Thus, in this study, the effect of two different concentrations of silicon, on the microstructure, hardness, modulus of elasticity and corrosion properties of the new TiMoZrxSi alloy has been investigated.

## 2. Experimental

### 2.1. Materials and samples preparation

The study of two compositional variants of new alloys with Ti, Mo, Zr and Si, namely from now on T1 (78 % Ti, 15 % Mo, 7 % Zr, 0 % Si) and T2 (77 % Ti, 15 % Mo, 7 % Zr, 1 % Si), has been carried out with the aim of applying different tests to find out their properties. The composition of the alloys was chosen based on the influence of the alloying elements, beneficial for titanium alloys with possible medical applications. Molybdenum (Mo) and silicon (Si), are  $\beta$ -stabilising elements that influences the decrease of modulus of elasticity. Zirconium (Zr), is a neutral element and exhibit the similar biomechanical characteristics to those of human bone. In the same way, silicon (Si) is a chemical element which is found in varying amounts in any structure of the body and is considered to be biocompatible with the body tissues.

The production of these alloys was carried out using a Vacuum Arc Remelting (VAR) furnace in which a consumable electrode was melted in vacuum at a controlled rate with the heat generated by an electric arc between the electrode and the ingot. To obtain a proper homogeneity of the alloys, they were turned and remelted in the VAR equipment for 6 times (3 times on each part) under an inert atmosphere of Argon and finally solidified into an ingot.

First, a series of previous steps were performed on the sample following the ASTM E3-11(2017) standard, such as chipping, cutting the samples for electrochemical and mechanical testing, grinding, and polishing. Then, both samples were mounted by adding a 4:1 ratio of epoxy resin catalyst in a mould, and they were demoulded after 24 h.

The samples were then cut 1 to 1,5 mm thick using the precision cutting machine IsoMet 4000 of Buehler, with an abrasive disc. For this purpose, the specimen was fixed by means of clamps and the machine parameters are selected. Afterwards, these cutted specimens were again mounted in order to carry out the corrosion and mechanical tests. Subsequently, the samples were roughed and polished with the Struers TegraPol-11 polisher in two stages: polishing with silicon carbide abrasive papers from 280, 400, 800, 1200, 2500 grit and final polishing with 0.1  $\mu$ m alpha alumina suspension to obtain a mirror finish polishing (Fig. 1). During the

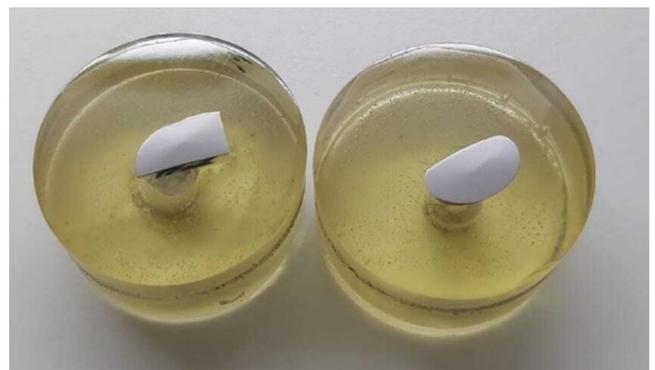


Fig. 1. Mirror-finished surface of samples.

process, the emery paper and polishing cloth had to be kept slightly damp to avoid breakage and wear of the paper due to friction between the grain and the sample and polishing was carried out in two batches for each sample. With this method, the surface deformation layers were removed and the structure of the material was exposed for subsequent metallographic analysis [31].

Finally, vertical cuts of approximately 2 mm thickness were made using again the cutting machine for the mechanical tests.

## 2.2. Microscope observations

The metallography technique has normally been used to show the spatial organization of the phases and compounds that make up a metallic material. For this reason, these tests have been the most suitable to know the constitution of the materials as well as to know the impurities, the orientation of the fibers or the mechanical defects that the samples may have.

To carry out this test, images were taken of the sample surfaces using the optical metallographic microscope Axio Vert.A1 MAT ZEISS, magnifying 5 times their real size. They were immersed in the Kroll reagent, which was composed of water, hydrofluoric acid and nitric acid, for 15 s and images were taken of the attacked surface.

## 2.3. Corrosion test

Corrosion test consisting of introducing a specimen into the electrochemical cell together with the saturated calomel electrode as reference electrode and the platinum electrode as counter electrode. The area of each sample was then calculated. These electrochemical studies were conducted in Ringer's solution, an isotonic solution normally composed of potassium chloride, sodium bicarbonate, calcium chloride and sodium chloride that resembles the plasma contained in human blood, which generally helps the body to balance its pH, muscle activation and the nervous system [32].

Two techniques were applied using the BioLogic Essential VSP potentiostat: Corrosion Potential and Electrochemical Impedance Spectroscopy.

**Corrosion potential.** The Mixed Potential Theory proposed by Wagner and Traud in 1938 [33] was followed, where oxidation and reduction reactions in electrochemical corrosion occur at the same rate on the metal surface. This technique together with the remaining technique required the use of the Ec-Lab software, "E<sub>corr</sub> vs Time" was selected and the necessary parameters such as the duration of 24 h were filled in. The data obtained was plotted as a graph of potential versus time.

**Electrochemical Impedance Spectroscopy (EIS).** This is a non-destructive method of measuring electrochemical impedance by applying an alternating current potential to an electrochemical cell and measuring the current through the cell. The response to this sinusoidal excitation potential is an alternating current signal that can be analyzed as the sum of sinusoidal functions. Therefore, this process was applied 7 times for each sample, at 7 different potential values in volts were added to or subtracted from the previously found corrosion potential by selecting in the software "Potentio Electrochemical Impedance Spectroscopy" and filling in the corresponding parameters, such as potential value or duration of 5 min. The data obtained were represented by means of Bode diagrams.

## 2.4. Three-point bending test

The three-point bending test was performed with the Bose ElectroForce® 3100 testing machine, based on ISO 7438:2020 and withstands up to 20 N of applied force. This test consisted of placing each rectangular section specimen, where the length of the specimens of the T1 sample was about 14 mm, while those of

the T2 were 13 to 12 mm, at the ends of the lower shank of the testing machine, leaving a sufficient distance between the supports, in this case, for the T1 of 9.72 mm and for the T2 of 7.80 mm. Then, a vertical load, with a linear velocity of 3 mm/s, was applied at the central point of the specimen until it exceeded the elastic limit or broke, in order to obtain its deformation. The values obtained for the applied force and the displacement of the specimens were collected in the form of a straight line, with their respective slopes, to calculate the modulus of elasticity.

## 2.5. Vickers microhardness

The Vickers microhardness of the alloys was measured by an indentation test using a REMET HX-1000 microhardness tester. The samples, with mirror polished surfaces for a good view of the indentations, were indented every 0.5 mm along the diameter. The tests were carried out according to ISO 14577-1:2015, applying a load of 50 g for 15 s. A minimum of 5 indentations were made on each sample and the average value was calculated and expressed as Vickers hardness (HV).

## 3. Results and discussions

### 3.1. Microstructure

The phase structure of an alloy is very important for the biocompatibility of samples and depends on the solubility of the alloying elements. By interacting the phase structure and the biological environment, the elements that are released and the body's response to the alloy can be determined [34].

For this reason, Fig. 2 shows the images of the surfaces of the 2 samples after electrochemical etching at x5 magnification.

It can be observed that both alloys have a dendritic structure but the sample with silicon addition has smaller and finer dendrites.

### 3.2. Corrosion test

**Corrosion potential.** Fig. 3 shows the graphs of corrosion potential ( $E_{corr}$ ) versus time of two TiMoZrxSi alloys immersed for 24 h in Ringer solution. After immersion, there was an abrupt displacement of the potential of the samples towards positive values for a period of 1–3 h. Subsequently, the open circuit potential continued to increase slowly in the case of the two alloys. Then, the potential continued to increase slowly for sample T1, while the potential of T2 tended to stabilize, suggesting the growth of a passive layer on the metal surface of both samples [35]. Also, T1 showed large irregularities in its potential curve between 60,000 and 80,000 s of test duration, due to movement of the test surface or loss of contact between the sample and the wire.

The corrosion potential value obtained from T1 was  $-194$  mV, being more positive than those found in previous studies of TiMoSi and TiMoZrTa alloys, while sample T2, with  $-308$  mV, presented similar values to TiMoSi [18].

**Electrochemical Impedance Spectroscopy (EIS).** Curves of the logarithm of the impedance modulus and the phase angle as a function of the logarithm of the frequency of samples T1 and T2 were plotted on the Bode diagrams.

In Fig. 4, the Bode impedance diagrams show a strong shift of the impedance modulus towards higher values, clearly indicating an increase in corrosion resistance due to the formation of the passive layer on the surface of the three materials. In the Bode phase curves, it was observed that the T1 and T2 processes occurred in a single phase and, as the potential increases, the film formed increases in thickness and has a capacitive response illustrated

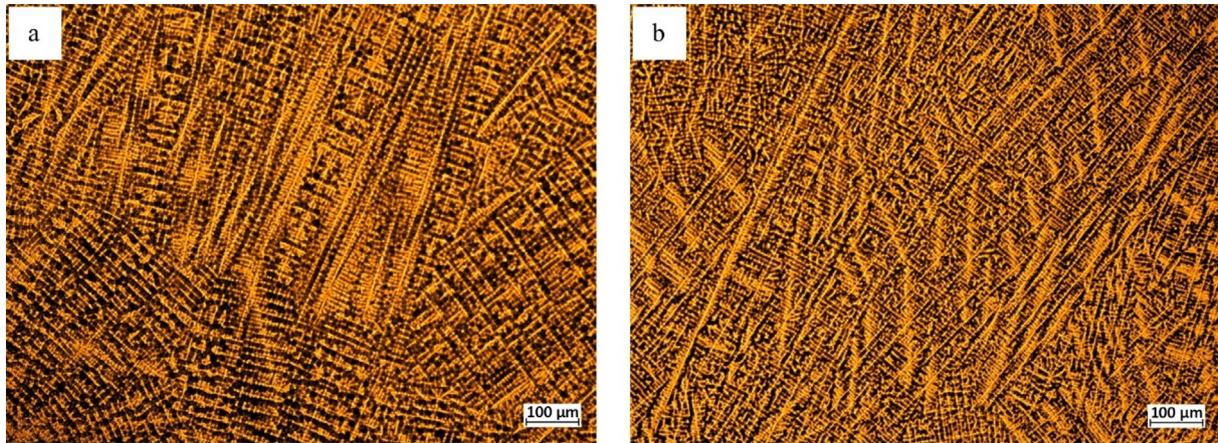


Fig. 2. Optical microstructure of samples T1 (a) and T2 (b) after reagent etching at x5 magnification.

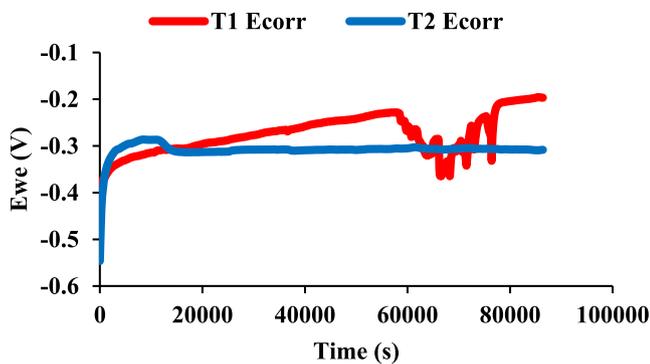


Fig. 3. Corrosion potential curves for T1(78Ti15Mo7Zr) and T2(77Ti15Mo7Zr1Si) after 24 h immersion.

by a phase angle close to  $90^\circ$  over a wide frequency range. This phenomenon is associated with an increase in capacitance (C), which is related to an increase in effective surface area [27].

Therefore, it was confirmed that the more positive the applied potential, the higher the impedance values and the phase angle. In this case, the values of the logarithm of the impedance were almost equal for both samples while the phase shift angles were higher for sample T2, so its corrosion resistance was higher.

### 3.3. Three-point bending test

For a comparative study, it was recommended to perform at least 3 tests per specimen. Table 1 shows the different specimens used for each variant, their dimensions, the support spacings used and the values obtained for the modulus of elasticity.

The average deviation is the arithmetic mean of the absolute values of the deviations from the average. On the other hand, the standard deviation indicates how spread out the data are from the mean. The standard error measures the precision of a population sample using the calculated standard deviation.

It has been observed that specimen T2 has used a smaller support spacing than T1, since the length of the specimens is shorter. For the same support spacing, the modulus of elasticity values of the three specimens of specimen T1 were far apart from each other from 70 GPa to 95 GPa. However, at T2, two specimens gave similar results from 62 GPa to 65 GPa, while the last one (T2.3) is 81 GPa. The mean value of the modulus of elasticity of sample T1 was 82.47 GPa, higher than that of sample T2, which was 69.56 GPa.

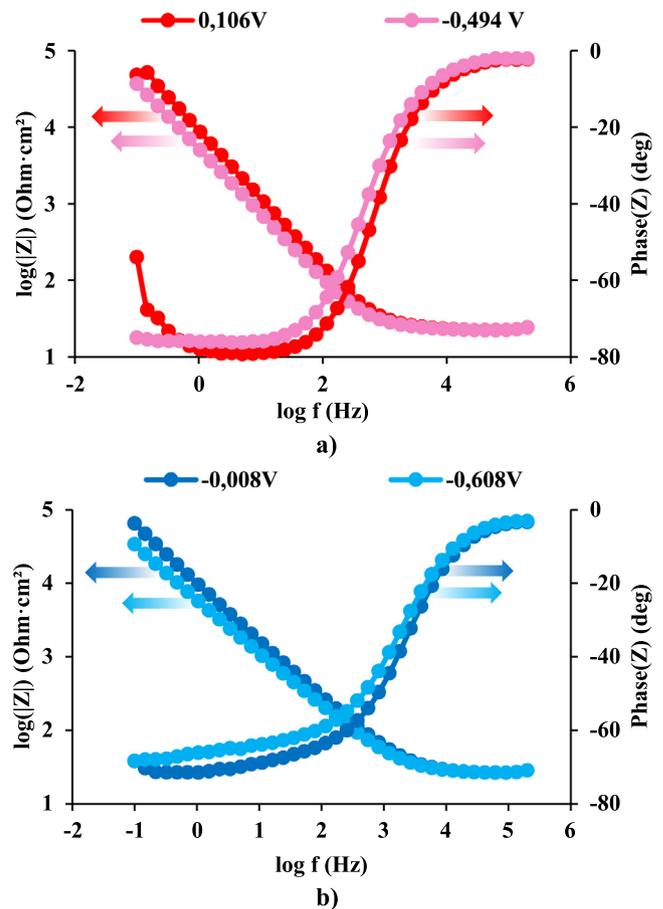


Fig. 4. Bode impedance and bode phase curves for T1(a) and T2(b) at  $\pm 300$  mV vs  $E_{corr}$  over 5 min.

Taking into consideration other metallic biomaterials such as CoCrMo alloys (210–253 GPa), titanium alloys Ti6Al4V (100–114 GPa) and stainless steels (190–210 GPa), the investigated titanium alloys exhibited lower and closer values to that of the human bone (17–30 GPa) [18].

According to the obtained results, the addition of Si on TiMoZr alloy decreases significantly the modulus of elasticity and in this way reduces the possibility of bone resorption and hence the failure of the implant [36].

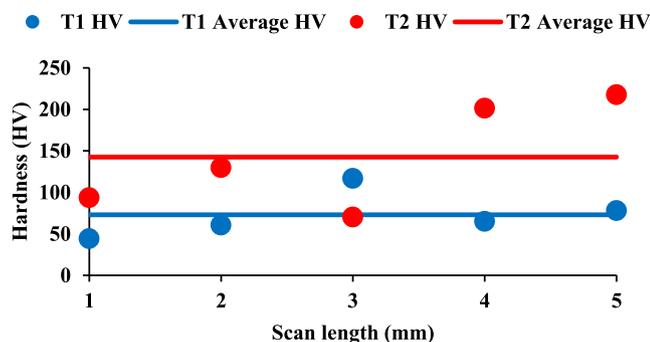


Fig. 5. Values obtained for T1(78Ti15Mo7Zr) and T2(77Ti15Mo7Zr1Si) Vickers microhardness and their mean for each indentation performed.

Table 1

Specimens tested with their modulus of elasticity average and standard deviations.

Sample	E Average (GPa)
T1	82.47 ± 12.81
T2	69.56 ± 10.04

### 3.4. Vickers microhardness

Fig. 5 shows the Vickers microhardness graph, as well as its mean, versus the sweep length obtained for a load of 50 g applied to each sample.

The Vickers hardness varied for each indentation performed due to the different hard and soft zones on the sample surfaces. Thus, the hardness values tended to increase with higher loads. In addition, the average Vickers microhardness obtained on the T2 sample is higher compared to that of T1.

In general, classical biomaterial alloys used for orthopaedics prosthesis, such as stainless steel and CoCrMo alloys, have hardness values between 155 HV and 601 HV. On the other hand, titanium alloys have values close to the Ti6Al4V alloy (349 HV), which is the alloy most used in implantology [18].

It can be observed that by adding 1 % Si to the TiMoZr alloy, the hardness increases reaching values of 150 HV which are comparable to that of the biomaterial 316 L (155 HV) [18].

## 4. Conclusions

In this study, the effects of silicon content on the microstructure, microhardness, modulus of elasticity and corrosion behavior of TiMoZrxSi alloy in a simulated body fluid were investigated, and the following conclusions were drawn:

- After the analysis of the results, it was confirmed, in the metallographic test, the two-phase structure of the T2 sample for the two types of polishing finishes used, while the T1 sample could not be attacked by the reagent.
- In the electrochemical tests, both samples tended to passivate, and it was demonstrated that the more positive the value of the applied potential, the greater the resistance to corrosion, presenting similar impedance values.
- As for the data obtained in the three-point bending test carried out for the different specimens, it was worth highlighting the differences among the 3 specimens of each sample, with higher values for sample T1, which did not have a silicon percentage. Finally, in the microhardness test, the T2 sample has a higher

Vickers hardness value and the indentations showed large differences in their peaks, so both samples had soft and hard zones due to the forming process.

- Therefore, it can be observed that the addition of 1 % silicon positively affects the properties of the material, since T2 presents both phases in its microstructure, has a good corrosion behaviour, the values of the modulus of elasticity are closer to those of human bone and has a higher Vickers microhardness.

The results presented above indicate that the structure and corrosion behaviour of TiMoZrxSi alloys strongly depend on the Si content, which is generally a good deoxidiser and improves the oxidation resistance.

Although further research on these new alloys is still needed, T2 shows, in principle, very good characteristics for the fabrication of hip replacements, superior to those of commercial alloys.

## CRedit authorship contribution statement

**Cristina Jiménez-Marcos:** Conceptualization, Methodology, Investigation, Writing – original draft. **Madalina Simona Baltatu:** Investigation, Methodology, Validation. **Néstor Rubén Florido-Suárez:** Formal analysis, Software, Validation. **Pedro Pablo Socorro-Perdomo:** Formal analysis, Resources, Visualization, Supervision. **Petrica Vizureanu:** Software, Validation, Investigation, Writing – review & editing. **Julia Claudia Mirza-Rosca:** Conceptualization, Validation, Investigation, Writing – review & editing.

## Data availability

No data was used for the research described in the article.

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Julia Claudia Mirza Rosca reports financial support was provided by University of Las Palmas de Gran Canaria.

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